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February 8, 1995

95-RF-01602

Kurt Muenchow
Environmental Restoration Division
DOE, RFFO

EVALUATION OF ARSENIC IN OPERABLE UNIT (OU) 5 AND OU 6 IN COMPARISON TO
BACKGROUND - CAB-014-95

Ref J M Roberson ltr, 08074, to S G Stiger, Interim Guidance on Operable Units 5 and 6
Risk Assessment Calculations, January 30, 1995

Action Review


This letter is in response to the referenced letter requesting a technical argument
supporting the exclusion of arsenic as a Chemical of Concern (COC) in OU5 and OU6

Attached is the evaluation of arsenic for groundwater, pond sediments, and stream sediments
for you review Arsenic was not considered a COC in other media Also, included is a spatial
distribution evaluation for arsenic on a sitewide level

OU 5 and OU 6 risk assessments are proceeding without arsenic included as a COC until
further guidance

Please review the attached information After your comments have been satisfactorily
resolved, this correspondence will be formally sent to the Department of Energy (DOE)

Should you have any questions or concerns regarding this issue, please call Neil Holsteen at
966-6987 or Carol Bicher 966-9100


Ed C Mast
Operable Unit No 5, 6 & 7 Closures
Environmental Restoration Program Division

CAB cb

Orig and 1 cc - K Muenchow

Attachment
As Stated

ADMIN RECORD

A-DU05-000617

DIST	LTR	ENC
AMARAL M E		
BURLINGAME A H		
BUSBY W S		
BRANCH D B		
CARNIVAL G J		
DAVIS J G		
FERRERA D W		
FRAY R E		
GEIS J A		
GLOVER W S		
GOLAN P M		
HANNI B J		
HARMAN L K		
HEALY T J		
HEDAH L T		
HILBIG J G		
HUTCHINS N M		
JACKSON O T		
KELL R E		
KUESTER A W		
MARX G E		
MCDONALD M M		
MCKENNA F G		
MONTROSE J K		
MORCAN R V		
POTTER G L		
PIZZUTO V M		
RISING T L		
SANDLIN N B		
SCHWARTZ J K		
SETLOCK G H		
STEWART D L		
STIGER S G		
TOBIN P M		
VOORHEIS G M		
WILSON J M		
G. B. BILMER		
N. A. HOLSTEEN		
A. J. RANDOL		
M. L. HOGG		
F. W. CHROMA		
CORRES CONTROL	X	X
ADMIN RECORD/080		
TRAFFIC		
PATS/T130G		

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SECRET	

AUTHORIZED CLASSIFIER
DOCUMENT SIGNATURE
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IN REPLY TO RFP CC NO

ACTION ITEM STATUS
PARTIAL/OPEN
CLOSED
LTR APPROVALS

ORIG & TYPIST INITIALS

RAB/cb

ARSENIC AT RFETS

DRAFT

During the January 25, 1995 meeting between DOE, RFFO and OUs 5 and 6 EG&G staff, DOE requested that EG&G provide technical information on the available process knowledge on arsenic usage at RFETS and an additional data evaluation for arsenic detected in OUs 5 and 6. The purpose of this letter is to provide this information.

Process Knowledge

As stated in the January 31, 1995 correspondence to Kurt Muenchow, DOE/RFFO, from Ed Mast, EG&G ERPD, EG&G reviewed the *Reconstruction of Historical Rocky Flats Operations & Identification of Release Points* (CDH, 1992) and the *Historical Release Report for the Rocky Flats Plant* (EG&G, 1992) and found no discussion of arsenic being used and/or released from any of the past processes at RFETS. Since then, an attempt was made to further document any possible uses of arsenic at RFETS, such as a pesticide for grasshopper control prior to the 1960s or 1970s. The ERPD librarian conducted an extensive search for references to arsenic in the sitewide databases. A majority of these references discussed arsenic as a sample analyte or within a general discussion of chemicals. One reference to the use of arsenic was as a chemical standard for the atomic absorption process in Building 771. However, no references were found indicating that arsenic was used in any large quantities at RFETS. Thus, it is unlikely that the arsenic detected in OUs 5 and 6 sediments results from onsite sources.

Arsenic Results in OUs 5 and 6

The arsenic results from environmental samples collected from OUs 5 and 6 are presented by medium in Table 1 and as follows:

Surface Soil, Subsurface Soil, and Surface Water Arsenic was not listed as a PCOC for any of these media in either OU5 or OU6.

Groundwater Initially, OU6 omitted total arsenic as a PCOC in groundwater samples using professional judgment, based primarily on the correlation between elevated metals concentrations and total suspended solids. Although EPA thought that this rationale "appears generally sound," they requested that DOE retain arsenic (as well as three other metals) as a COC in groundwater based on the fact that the maximum OU6 concentration is 18 $\mu\text{g/l}$ and the PRG is 0.0038 $\mu\text{g/l}$. DOE agreed to handle this issue for OU6 in the same way as OU2. OU2 had received conditional approval on their COC TM with the understanding that a quantitative risk assessment will be conducted for arsenic in groundwater and the results included in the uncertainty analysis (rather than in the risk characterization) section of the HHRA. The risk from these metals, including arsenic, would not be added in with the risks

from the other groundwater COCs. In light of the current discussions regarding arsenic, DOE may also want to rethink this agreement with the agencies.

In the OU5 COC TM, arsenic was determined to be a COC for groundwater. The Gilbert Methodology statistical tests were not run for this constituent, due to the low frequency of detection (12%) for total arsenic in background groundwater from the Upper Hydrostratigraphic Unit (UHSU). The concentrations of total arsenic detected in wells within OU5 were compared to the background normal UTL_{99/99} (8.2 µg/l) for total arsenic instead of the lognormal UTL_{99/99} (19.3 µg/l) because the Background Geochemical Characterization Report (DOE, 1993) presented normal UTL values. Most naturally occurring elements are not normally distributed (Isaaks and Srivastava, 1989, EPA 1992), therefore, a comparison of the OU5 maximum concentration (13.3 µg/l) to the lognormal UTL_{99/99} may be more realistic. The lognormal UTL comparison indicates that arsenic is not a COC in groundwater in OU5. Furthermore, calculation of statistical parameters for data sets with greater than 80% nondetects are invalid, and those between 50-80% nondetects are questionable (Helsel, 1990, Gilbert and Simpson, 1992).

The maximum concentrations reported in background groundwater for total and dissolved arsenic were 7 and 15 µg/l, respectively (DOE, 1993). Although one would generally expect the maximum for "totals" to exceed that for "dissolved" (Hem, 1992), the inherent variability in sampling analysis leads to occasional exceptions, as in this case. All measurements of arsenic (total and dissolved) in OU5 groundwater are less than the maximum background value of 15 µg/l for dissolved arsenic in background UHSU groundwater.

Metal concentrations in water are analyzed for both total (unfiltered) concentrations and dissolved (filtered) concentrations. Depending on the amount of suspended solids in the sample, these two analyses may yield very different results. In OU5, the maximum concentration of unfiltered arsenic in groundwater was 13.3 µg/l, while that for filtered arsenic was 8 µg/l. In OU6, the maximum level for unfiltered arsenic was 18 µg/l and for filtered was 4 µg/l. Since, in general, unfiltered concentrations for metals in groundwater are higher values, these are used in risk assessment in keeping with the philosophy of using the most conservative data to estimate risks.

Pond Sediments Arsenic was determined not to be a COC in OU6 for this medium. Although arsenic was listed as a COC for pond sediments in the OU5 COC TM, further examination of statistical comparisons indicated that the OU5 data were compared to background stream sediments as well as seep/spring sediments due to the absence of background data for pond sediments. However, pond sediment data should have been compared to only background seep/spring data because they are both a zone of accumulation as opposed to stream sediments which are "in transport." None of the statistical tests indicated a significant difference in arsenic in OU5 sample data versus seep/sediment background samples.

Stream Sediments The only statistical test that indicated a significant difference in the populations of data in OU5 and OU6 samples versus background was the Gehan test. Due to the very small sample size for the OU data (n=8 for OU5, n=15 for OU6), and the apparent large number of nondetects in the background arsenic results, the results of the Gehan test need to be evaluated carefully. The Gehan test is evaluated below.

The attached RFETS maps show the distribution of arsenic in stream sediments, pond sediments, and surface soils onsite and expanded offsite to include the OU3 reservoirs. The various color codes and values shown in the legend are the UTLs_{99/99} for these specific media: 10.1 mg/kg for stream sediments, 12.9 mg/kg for surface soils, and 66.7 mg/kg for pond sediments.

Evaluation of Gehan Statistical Test

EG&G examined the statistical comparison of the OUs 5 and 6 stream sediment results to background. For stream sediments, as well as other media, the one test that was predominantly failed is the Gehan test. Although the Gehan test was proposed as a way to deal with multiple detection limits and is not supposed to be sensitive to sample size or number of nondetects, there is some concern regarding the validity of this statistical test when comparing data sets with small sample sizes or a large percentage of nondetects.

Helsel (1990) notes that, "In the most comprehensive review of these score tests (such as the Gehan), most of them were found inappropriate for the case of unequal sample sizes" (See Attachment A). Gilbert himself cautioned us about the use of the untested and unproven Gehan test. Gilbert (1993) noted, "As the performance of the Gehan test has not, in my opinion, been adequately determined, I recommend that statistical evaluations and comparisons of its performance with competing tests should be conducted by EG&G at the earliest time." Competing tests include the Wilcoxon Rank Sum and Kruskal-Wallis tests, which, according to Gilbert, "are very well known by statisticians and practitioners, and are widely used in many fields of application" (Attachment B).

An evaluation of Gilbert's recommendations, including comparative testing of the Gehan test, was prepared by Dr. Kenny S. Crump, ICF Kaiser, at the request of EG&G Rocky Flats. Dr. Crump (1993) states as one of his conclusions that "For data containing nondetects, Gilbert recommends the *ad hoc* approach of applying the slippage and quantile tests to the ranks calculated in connection with the Gehan test rather than to the actual data. This *ad hoc* procedure is invalid and can produce nonsensical results. Consequently, it should not be applied under any conditions."

Weight of Evidence

Attachment C provides a series of tables showing the ranges of arsenic in rocks, surface soils, and sediments. It should be noted that "the northern and southern parts of the (Front Range)

Corridor are underlain by marine shale, which typically contain larger amounts of trace elements " (Severson and Tourtelot, 1994) As seen in these tables, the values of arsenic found at RFETS are well within levels for background

Summary and Conclusions

Gilbert (1993), in describing Phase V of his statistical methodology, recommended the use of professional judgement in determining the validity of the background comparisons His basic questions are (1) Do the results of the statistical tests make sense in light of what is known about the geology, hydrology, and geochemistry of the OU? and (2) Are the assumptions underlying the statistical tests valid? Gilbert also recommended a review of historical information on the operation of RFETS to determine consistency of that information with statistical test results

In summary of the information provided above, the following statements can be made concerning the source of arsenic in OUs 5 and 6 environmental samples, particularly stream sediments, at RFETS

- 1 No large quantities of arsenic have been released or used in past RFETS process activities to act as a source
- 2 Arsenic was not determined to be a COC in surface soils, subsurface soils, surface water, and pond sediments
- 3 The validity of using the Gehan test for these types of comparisons is questionable
- 4 Review of numerous literature sources suggests that arsenic concentrations detected at RFETS are well within background for the region

The application of professional judgment to evaluate the source of arsenic at RFETS supports the conclusion that arsenic detected in stream sediments, as well as other media, of OUs 5 and 6 should be considered as background values

Table 1

SUMMARY OF ARSENIC DATA FOR OU5 AND OU6					
Medium	OU5 Results		OU6 Results		
	Mean	Maximum	Mean	Maximum	
Surface Soil (mg/kg)	4 6	8 9	5 3	11 0	
Subsurface Soil (mg/kg)	3 9	18 9	3 6	10 9	
UHSU Groundwater - total (ug/l)	5 6	13 3	4 6	18 0	
UHSU Groundwater - dissolved (ug/l)	4 1	8 1	3 9	4 0	
Surface Water - total (ug/l)	4 4	5 7	4 7	6 6	
Surface Water - dissolved (ug/l)	4 8	3 6	4 8	7 4	
Seep Water - total (ug/l)	10U	10U	NA	NA	
Seep Water - dissolved (ug/l)	NA	NA	NA	NA	
Pond Sediments (mg/kg)	5 5	9 8	6 0	10 2	
Seep Sediments (mg/kg)	5 7	6 5	NA	NA	
Stream Sediments (mg/kg)	3 5	5 5	3 6	5 8	
U = Not detected					
NA = Samples not taken in this medium					

Source: Bruce A Fowler, Biological and environmental effects of arsenic

Arsenic fluxes between geochemic reservoirs

Flux	Magnitude (10 ⁶ g/yr)
From land to	
terrestrial biota	282.8
atmosphere (vapor)	210
atmosphere (continental dust)	25
ocean (river suspended)	2.380
ocean (river dissolved)	612
atmosphere (emission)	779.3
Atmosphere to	
land (rain)	970
land (dust)	8
ocean (rain)	1.970
ocean (dust)	17
Ocean to	
atmosphere	1.947.9
In ocean	
skeletal to sediments	29.4
dissolved to biota	1.080
biota to particulate	38.9
biota to dissolved	1.041.1
dissolved to skeletal	344.5
skeletal to dissolved	115.1
particulate to sediment	2.435.9
Terrestrial	
biota to land	292.8
Volcanic to	
atmosphere (vapor)	0.1
atmosphere (dust)	2.7
sediments (oceanic)	40
land	54
Sediments to	
land	2.400
Mining	455

a Data from Mackenzie et al (1979)

Arsenic in rocks

Igneous rocks	No. analyses	Arsenic concentration (ppm)	
		Range usually reported	Average
Ultrabasic	37	0.3 - 16	1.0
Basaltic gabbros	146	0.06 - 113	2.0
Andesites dacites	41	0.5 - 5.8	2.0
Granitic	73	0.2 - 13.8	1.5
Silicic volcanic	52	0.2 - 12.2	3.0
Sedimentary			
Limestones	37	0.1 - 20	1.7
Sandstones	11	0.6 - 120	2.0
Shales and clays	324	0.3 - 490	14.5 ^a
Phosphorites	982	0.4 - 108	22.0
Sedimentary iron ores	110	1 - 2,900	400
Sedimentary in igneous ores	-	(up to 1.5%)	
Coal	1,150	0 - 2,000	13

a Estimated on the basis of data of Onishi (1969) and Boyle and Jonasson (1971)

b Excluding one sample with arsenic at 490 ppm

c Boyle and Jonasson (1973) gave 4 ppm

Arsenic concentrations in sediments and biota of freshwater ecosystems

Author	Location	Range of sediment arsenic concentrations (mg/kg)	Range of A _s concentrations in biota	aquatic organisms
Tsai et al 1979	Baltimore Harbor U.S.A.	13 - 229 ^a	ND	ND
Reay 1972	Waikato River New Zealand	76 - 450 ^a	8 - 971 (plants)	ND
Lancaster et al 1971	Lake Arapuni Lake Ohakuri	ND	215 - 1,450 (likeweed)	ND
Greichus et al 1978	Lake Mchillwane Zimbabwe	37 ^a	2.9 ^a (plankton)	1.3 - 6 ^a (oligochaetes, benthic insects, fish)
Price and Knight 1978	Lake Washington Mississippi and Sardinia Reservoir U.S.A.	2.99 ^a	21.74 (plankton)	0.41 (clams)
Kobayashi and Lee 1978	Brown Lake Wisconsin U.S.A.	4 - 107 ^a	ND	ND
Hett et al 1980	Lake George New York U.S.A.	1.1 ^a	ND	0.2 - 0.3 ^a (mussels)
Ruppert et al 1974	Chautauque New York U.S.A.	<0.5 - 106 ^a	ND	ND
Wagemann et al 1978	Kam Lake Northwest Territories Canada	40 - 1,500 ^a	250 - 970 ^a (plants)	0 - 820 (polychaetes, oligochaetes, ephemeroptera, trichoptera, chironomidae, zooplankton, hemiptera, diptera, hirudinea, fish, amphipoda)
Lucas et al 1970		ND	ND	
Pakkala et al 1972		ND	ND	

a Wet weight basis

b Dry weight basis

ND = not determined

Table 42 Element composition of the earth's crust and sediments (major elements in %, minor and trace elements in $\mu\text{g/g}$)

Element	Mean crust	Mean sediment ^b	Average shale ^c	Deep sea clay	Shallow water sediment ^d	River suspended sed. ^e	Sandstone ^f	Limestone ^g	Soil ^h
Silicon	27.7%	24.5%	27.5%	25.0%	2.0%	28.5%	12.7%	1.2%	310%
Aluminum	8.2%	7.2%	5.0%	8.4%	6.4%	9.4%	4.5%	0.7%	67%
Iron	4.1%	4.1%	4.7%	6.5%	6.5%	4.8%	2.9%	1.7%	3.2%
Calcium	4.1%	6.6%	2.2%	2.9%	2.9%	2.2%	3.1%	14.0%	20%
Magnesium	2.3%	1.4%	1.5%	2.1%	2.1%	1.2%	1.2%	0.6%	0.8%
Sodium	2.3%	0.6%	1.0%	4.0%	4.0%	0.7%	1.0%	0.1%	1.1%
Potassium	2.1%	2.0%	2.7%	2.5%	2.5%	2.0%	1.5%	0.1%	1.8%
Titanium	0.6%	0.1%	0.5%	0.5%	0.5%	0.6%	0.4%	0.01%	0.5%
Phosphorus	1.00%	670	700	1.500	550	1.150	440	700	800
Manganese	0.50	770	650	6.700	850	1.050	460	620	760
Barium	500	460	550	2.100	-	600	320	90	568
Strontium	370	320	140	110	160	150	320	610	278
Zirconium	190	150	160	150	210	-	220	20	345
Vanadium	160	105	110	120	145	170	35	45	108
Chromium	100(?)	72	90	90	60	100	20	11	84
Nickel	80(?)	52	68	250	35	90	10	7	34
Zinc	75	95	95	165	92	350	30	20	60
Copper	50	33	45	250	56	100	0.3	51	26
Cobalt	20	14	19	74	13	20	38	0.1	12
Lithium	20	56	66	57	77	25	1	7.5	31
Scandium	16	10	13	19	12	18	1	1	10
Lead	14	19	20	50	22	150	10	57	29
Cesium	3.0	4.2	5	6	-	6	0.5	0.5	3
Beryllium	2.6	2	3	2.6	3	-	< 1	1	15
Uranium	2.4	3.1	17	13	-	1	0.5	2.2	2.2
Tin	2.2	4.6	60	15	2	-	0.5	0.5	58
Molybdenum	1.5	2.0	2.6	27	1	3	0.2	0.2	19
Arsenic	1.5	7.7	13	13*	5	5	1	1	11.3
Tungsten	1.0	1.7	18	11*	-	-	1.6	0.6	11
Antimony	0.2	1.2	1.5	10	-	2.5	0.05	0.3	1.7
Cadmium	0.11	0.17	0.22*	0.42	-	1	0.05	0.03	0.6
Silver	0.07	0.06	0.07	0.11	-	-	0.25	0.12	0.4
Mercury	0.05	0.19	0.18*	0.08	-	-	0.29	0.16	0.1
Selenium	0.05	0.42	0.06	0.17	-	-	< 0.01	< 0.03	0.4

* Bowen (1979)

* Bowen (1979) after Wedepohl (1968)

* Turckin and Wedepohl (1961)

* Bowen (1979) after Wedepohl (1968, 1969, 1971)

* Marowski and Wedepohl (1971)

* Uric and Barrow (1982)